PB-244 885

EFFECT OF CHEMICAL COMPOSITION ON SURFACE RESISTIVITY OF FLY ASH

R. E. Bickelhaupt

Southern Research Institute

Prepared for:

Environmental Protection Agency

August 1975

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August 1975

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TECHNICAL REPORT DATA
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1. REPORT NO. EPA-600/2-75-017	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Effect of Chemical Composition on Surface Resistivity of Fly Ash		5. REPORT DATE August 1975 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. E. Bickelhaupt		8. PERFORMING ORGANIZATION REPORT NO. SORI-EAS-75-397 3134-XV
9. PERFORMING ORGANIZATION NAME AND ADDRESS Southern Research Institute 2000 Ninth Avenue South Birmingham, Alabama 35205		10. PROGRAM ELEMENT NO. 1AB012; ROAP 21ADJ-029 11. CONTRACT/GRANT NO. 68-02-1303
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final: 4/74 - 4/75 14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES		

16. ABSTRACT The report gives results of a study of the effect of chemical composition on the surface resistivity of fly ash. The resistivity of a group of well characterized fly ashes was determined. Resistivity data were taken between 60 and 250 C in an environment of air containing approximately 9 vol. % water. Chemical transference experiments were conducted for two ashes with substantially different chemical compositions. Chemical analyses of the transference specimens revealed a pronounced migration of alkali metal ions toward the negative electrode: the surface resistivity was inversely proportional to the concentration of these ions. Ion concentration influenced the participation of potassium in the current conduction process. Surface resistivity is sensitive to the chemical composition of fly ash because the alkali metals serve as charge carriers. The conduction mechanism is probably analogous to that of glass. This viewpoint is compatible with the usual empirical observations regarding the effect of certain parameters on resistivity; for example, the interaction between ash and the environment.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Fly Ash Surface Resistivity Chemical Composition	Air Pollution Control Stationary Sources	13B 21B 20C 07D

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Unlimited	Unclassified	52
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

EPA-600/2-75-017

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by

R. E. Bickelhaupt

Southern Research Institute
2000 Ninth Avenue South
Birmingham, Alabama 35205

Contract No. 68-02-1303
ROAP No. 21ADJ-029
Program Element No. 1AB012

EPA Project Officer: Leslie E. Sparks

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, North Carolina 27711

Prepared for

U. S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D. C. 20460

August 1975

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Publication No. EPA-600/2-75-017

THE EFFECT OF CHEMICAL COMPOSITION ON THE SURFACE RESISTIVITY OF FLY ASH

ABSTRACT

Resistivity was determined for a group of well characterized ashes representing both Eastern and Western coals. Data were taken between 60°C and 250°C in an environment of air containing approximately 9 volume percent water. Chemical transference experiments were conducted for two ashes having substantially different chemical compositions.

Chemical analyses of the transference specimens revealed a pronounced migration of alkali metal ions toward the negative electrode. It was observed that the surface resistivity was inversely proportional to the concentration of these ions and that the iron concentration influenced particularly the participation of potassium.

Surface resistivity is sensitive to the chemical composition of fly ash because the alkali metals serve as charge carriers. The conduction mechanism is probably analogous to that of glass. This viewpoint is compatible with the usual empirical observations regarding the effect of certain parameters on resistivity; for example, the interaction between ash and the environment.

This report was submitted in partial fulfillment of Contract No. 68-02-1303 by Southern Research Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of October 1974.

CONTENTS

		Page
Abstract		ii
List of Figures		iv
List of Tables		v
Acknowledgement		vi
Sections		
I	Conclusions	1
II	Recommendations	2
III	Introduction	3
IV	Scope	5
V	Experimental Equipment, Procedures and Calculations	6
VI	Results	16
VII	Discussion	30
VIII	References	36
Appendix A		38

FIGURES

No.		Page
1	Schematic of Apparatus Set-Up for Resistivity Measurements	8
2	Photograph of General Apparatus Set-Up for Resistivity Determination	9
3	Photograph of Environmental Chamber and Oven	10
4	Photograph of Environmental Chamber and Electrode Set	12
5	Typical Resistivity Data as a Function of Reciprocal Absolute Temperature	22
6	Maximum Surface Resistivity Versus the Combined Atomic Percentage of Lithium and Sodium	25
7	Maximum Surface Resistivity Normalized to 0.4 Atomic Percent Lithium Plus Sodium Versus Potassium Concentration	26
8	Maximum Surface Resistivity Normalized to 0.4 Atomic Percent Lithium Plus Sodium Versus Iron Concentration	28
9	Maximum Surface Resistivity Normalized to 0.4 Atomic Percent Lithium Plus Sodium Versus Combined Potassium and Iron Concentrations	29
10	Correlation Between Estimated and Measured Maximum Surface Resistivity	34
11	Surface Resistivity and Soluble Sulfate as a Function of Surface Area	41

TABLES

No.		Page
1	Chemical Analyses of Ashes in Weight Percent	17
2	Miscellaneous Ash Characteristics	18
3	Chemical Analyses of Transference Experiments in Weight Percent	20
4	Characterization of Fractionated Fly Ash	39

ACKNOWLEDGEMENT

Other Southern Research Institute employees who participated in this research include Mr. W. R. Dickson and Mr. Johnny Sutherland - chemical analysis of the ashes, and Mr. C. A. Reed - physical characterizations and resistivity measurements.

SECTION I
CONCLUSIONS

Surface conduction occurs by an ionic mechanism involving the interaction between the continuous matrix of glassy particulates and the environment. Transference experiments revealed that the alkali metal ions serve as charge carriers; however, the possibility of other ions participating as charge carriers was not excluded. It was concluded that the attack by certain environmental species, water and acid, on the surface of the glassy ash mobilizes the alkali metal ions.

A correlation was established between the magnitude of maximum surface resistivity and the concentrations of lithium, sodium, potassium and iron. It was speculated that the role of iron is related to the structure and/or chemical durability of the ash, thereby influencing the degree of participation of the alkali metal ions, particularly potassium. The correlation offers a possible means of estimating the resistivity of an ash from the chemical analysis for a given set of environmental conditions.

It was observed that the measured resistance of an ash layer is inversely proportional to a parameter defining the surface area of the ash when surface conduction is important. The magnitude of this effect among ashes is large enough so that it should be considered in the study of resistivity as a function of the other factors of influence.

SECTION II
RECOMMENDATIONS

Using a research approach generally similar to that reported herein, other factors that influence the surface resistivity of fly ash should be investigated with the objective of incorporating additional parameters into a procedure for predicting the magnitude of resistivity. Specifically, a study should be made of the effect of field strength and variations in the environmental parameters. Environmental conditions of interest should include a simulated flue gas with variable concentrations of water, sulfur trioxide, and sulfur dioxide.

It has been shown that several physical and chemical characteristics of an ash influence resistivity. This knowledge should be expanded to include a study of the chemical dissolution of ash as a function of the environmental parameters. Such a study would help one objectively select conditioning agents.

It is believed that the ability to predict fly ash resistivity from the chemical composition of commercial ashes for defined conditions has progressed sufficiently to warrant a study leading to the prediction of this value from the analyses of coal and coal ashes produced in a laboratory.

SECTION III
INTRODUCTION

Electrical resistivity is one of the critical parameters influencing the collectability of fly ash by electrostatic precipitation. This report discusses research designed to acquire additional knowledge about the surface conduction process. The immediate objective of the work reported herein was to study surface resistivity of fly ash with respect to the conduction mechanism and the effect of the chemical composition. The ultimate pragmatic objective of this research is to obtain sufficient information so that resistivity might be predicted from the measurable chemical factors and conditioning agents might be objectively selected.

At temperatures of 450°C down to 250°C or for certain conditions as low as 200°C, the volume resistivity of fly ash is dependent on an ionic conduction mechanism in which sodium ions serve as the principal charge carriers.[1] For a given ash chemistry, the volume resistivity is also dependent on ash layer porosity, field strength and temperature.

Over some range of temperature from perhaps as low as 125°C to as high as 250°C, both volume and surface conduction mechanisms contribute to the measured value of resistivity. Below 125 to 150°C, the resistivity is principally controlled by surface conduction. The factors that are assumed or known to influence the magnitude of surface resistance include: the chemical species that make up the environment of the ash, the temperature, the chemical composition of the ash, the surface area of the ash, and the field strength. Surface conduction results from the interaction of the environment and the ash surface.

It has been generally accepted[2] that surface conduction occurs by an electrolytic or ionic mechanism dependent principally on the physical and chemical adsorption of certain species on the ash surface to produce a conducting film. This implies that conduction is governed by the electrolysis of the adsorbed species and that the component ions serve as charge carriers.

Since the principal microconstituent of fly ash is a glassy particulate, it is possible that surface conduction occurs in a manner similar to that of glass. In this case, conduction would take place by an ionic mechanism in which alkali metal ions serve as the principal charge carriers. The role of the environment would not be lessened since the interaction between the ash surface and environment is required to mobilize the carrier ions.

This research attempts to obtain information concerning the surface conduction mechanism and determine the influence of the chemical composition of fly ash on resistivity.

SECTION IV
SCOPE

Seventeen commercially produced fly ashes representing a cross-section of Eastern and Western coals were utilized. These ashes were chemically and physically characterized with respect to certain properties known to influence resistivity. Using an ASME, PTC 28 electrode set, the surface resistivities were determined at a voltage gradient of ∿ 400 volts/cm in an environment of air containing ∿ 9 volume percent water over a temperature range of 60°C to 250°C. Chemical transference experiments were conducted for two ashes having similar values of resistivity but dissimilar chemical compositions. The effect of particle size (conducting surface area) on resistivity was examined for one ash elutriated to five size fractions.

SECTION V
EXPERIMENTAL EQUIPMENT, PROCEDURES AND CALCULATIONS

SPECIMEN SELECTION AND ASH CHARACTERIZATION

The ashes were received from commercial steam generating power plants. With few exceptions, the manner in which the sample was acquired and the sampling location was not known. After passing the ash through an eighty mesh screen to remove large foreign objects, the incoming sample was quartered to yield eight equivalent, random specimens weighing about 25 grams each. These specimens were used for resistivity measurements, chemical transference determinations and ash characterization.

The ashes were characterized for chemical composition, helium pycnometer density and particle size distribution. Helium pycnometer density was determined with a Micromeritics Instrument Corporation, Model 1302 helium-air pycnometer using the manufacturer's suggested procedures. A number 6000 Bahco Micro Particle Classifier was employed to determine the particle size distribution using the technique outlined by the manufacturer. Density and particle size data were used to calculate resistivity-specimen porosity and a factor to represent the variation in ash surface area. Chemical analyses were conducted for the elements commonly reported for fly ash. Three methods of attack are required to prepare fly ash for a complete chemical analysis. Digestion in H_2SO_4 - HF-HNO_3 provides a sample for the determination of Li, Na, K, Ca, Mg, Fe, and Ti by atomic absorption spectrophotometry and P by a colorimetric method. Colorimetric procedures are also used for the analysis of Al and Si following fusion of fly ash in sodium hydroxide. The total sulfate content is determined turbidimetrically after fusion of the fly ash in sodium carbonate.

EXPERIMENTAL SET-UP FOR RESISTIVITY DETERMINATION

Resistivity was determined in the temperature range of 60°C to 250°C in a controlled environment of air and water vapor. The general appearance of the experimental arrangement is shown schematically and photographically in Figures 1 and 2 respectively. Tank air was metered to provide about 9 volume changes per hour in the environmental chamber. The air was passed through a glass, fritted-disc bubbler submerged in a constant temperature water bath. Water bath temperature could be controlled to $\pm$ 0.5°C. Air passing through the distilled water in the bubbler was approximately saturated with respect to the temperature of the constant temperature bath. The air-water mixture was passed through an externally heated stainless steel tube into the environmental chamber where the gas was diffused by a glass, fritted-disc. The gas stream was directed toward the bottom of the environmental chamber and exited out the top through an externally heated tube that also provided a position for sampling the gas. Once during every test the gas stream was sampled to gravimetrically determine the water content. Typically the gravimetric determination showed a water concentration of 9.5 volume percent when the equipment was set to deliver 10.0 volume percent.

The stainless steel environmental chamber was housed in a conventional laboratory oven as shown in Figure 3. All feedthroughs and connecting surfaces were sealed with high temperature O-rings. The simple on-off thermal control that was standard for the oven was disconnected, and a three-mode, solid state device was used to control the temperature of the oven. A control thermocouple in contact with the base of the chamber was maintained within $\pm$ 1°C.

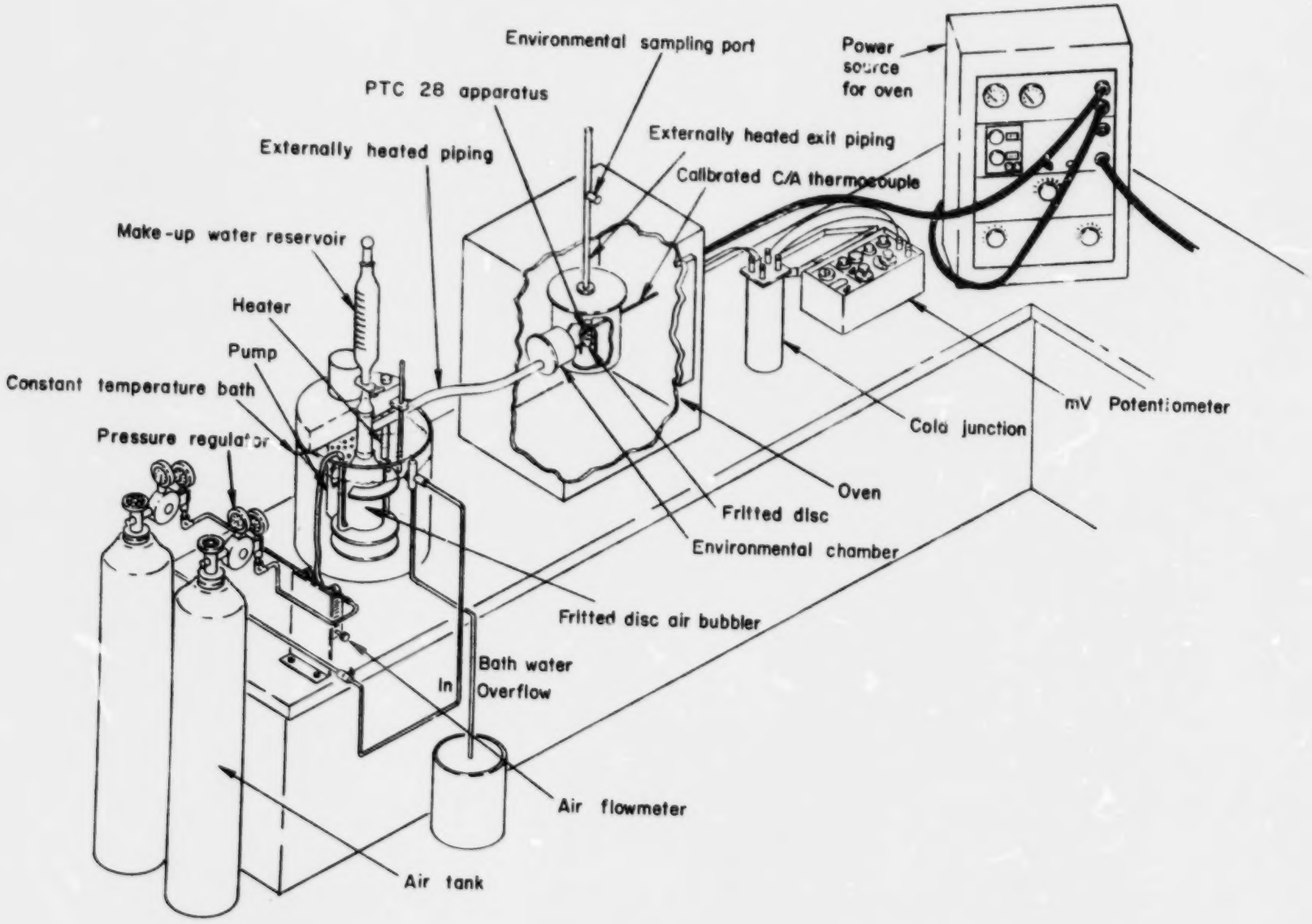

Figure 1. Schematic of Apparatus Set-up for Resistivity Measurements

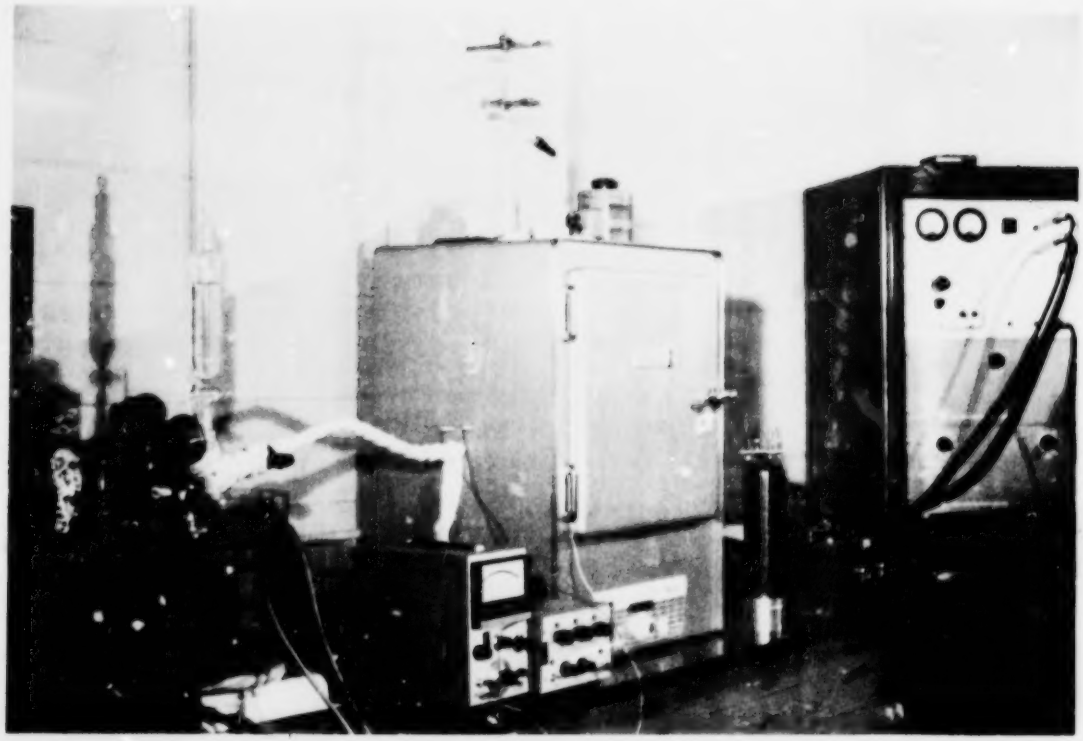

Figure 2. Photograph of general apparatus set-up for resistivity determination

Figure 3. Photograph of environmental chamber and oven

Resistivity was measured using the ASME PTC-28 apparatus[3] shown placed in the environmental chamber in Figure 4. Clip-on electrical leads are shown with the electrode set resting on alumina supports. The air-water vapor mixture was dispersed downward beneath the lower, stainless steel, fritted disc electrode. Specimen temperature was determined with a calibrated, sheathed thermocouple that was positioned a few mm above the upper surface of the ash. The test circuit included a Keithley Model 240A high voltage supply and a Keithley Model 610 electrometer.

TEST PROCEDURE FOR RESISTIVITY MEASUREMENT

Description

The weight and volume of the dish-shaped lower electrode was determined so that specimen porosity could be calculated using the helium pycnometer density of the ash. Electrode sets were ultrasonically cleaned in a commercial cleaning solution, rinsed in water, rinsed in alcohol and dried before each test. The ash specimen was poured into the dish-shaped electrode with occasional tapping of the edge and bottom of the electrode. Excess ash was leveled to the upper lip of the dish using a straight edge. The tapping action inhibited bridging of the particles and yielded a specimen into which the upper electrode did not readily sink. After weighing the lower electrode containing ash, the upper electrode was placed in position, and the assembly was set on the alumina supports in the environmental chamber. The following steps were taken: internal connections were made, the top sealed in position, the chamber placed in the oven, external connections were made and the oven was closed for test. The environmental chamber was allowed to thermally equilibrate overnight at 60°C. Externally heated inlet and outlet tubing and the constant

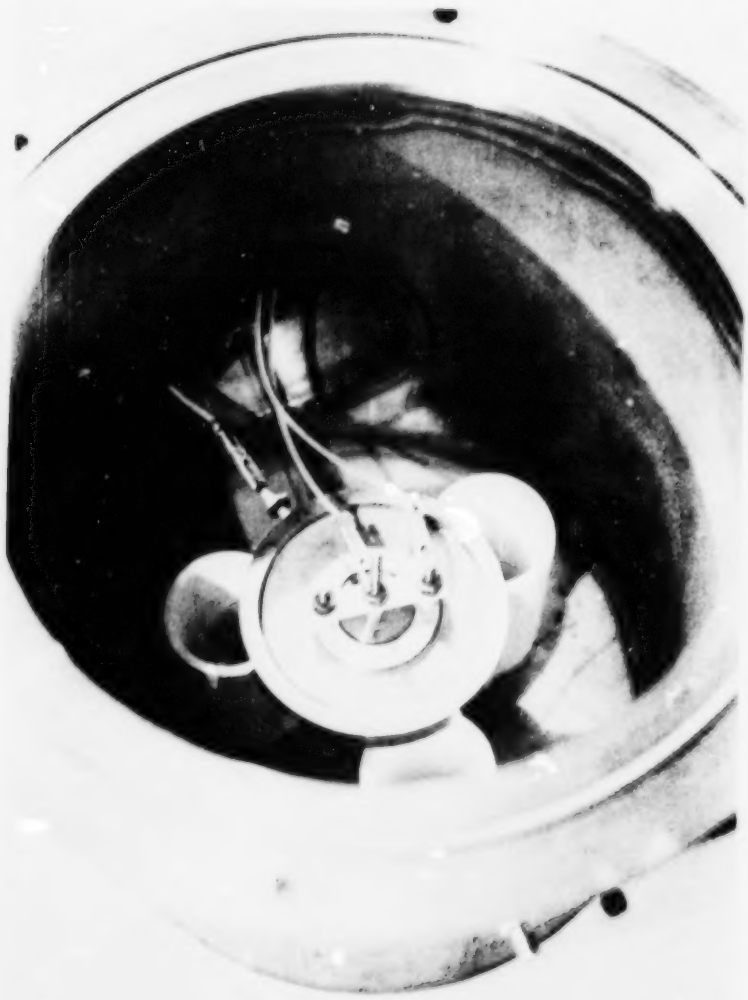

Figure 4. Photograph of environmental chamber and electrode set

temperature water bath were automatically started about two hours prior to the beginning of the test.

Two hundred volts dc were applied to the resistivity specimens, and current versus time was monitored. When the current was decreasing at a rate less than 10% in 10 minutes, it was assumed to be stable. The time required to reach current stability varied from 10 to 30 minutes among ashes. After the current had stabilized, the applied voltage was removed, and the air-water environment was introduced. Every ten minutes thereafter the voltage was reapplied and the current read after one minute. The current increased about 3 or 4 orders of magnitude due to the introduction of the air-water mixture and was stable after 20 to 40 minutes. The major portion of the current increase took place in the first ten minute increment. The stabilized current reading with the air-water mixture flowing was used to calculate resistivity at 60°C.

The temperature set point was then advanced for the next data point, 80°C. Temperature increase at the position immediately above the ash specimen was observed. When the rate of temperature rise was less than 1°C/5 minutes, the voltage was applied and current read one minute later. The application of voltage and reading of current was repeated after an additional 15 and 30 minutes. The temperature set point was then increased to the next level. In this manner resistivity was determined for six temperatures: about 60, 80, 110, 140, 180, 220 and 260°C.

It was believed that the procedure was satisfactory for the main objective of this work; i.e., the evaluation of surface resistivity as a function of ash composition.

TEST PROCEDURE FOR CHEMICAL TRANSFERENCE

Chemical transference experiments were run using the resistivity test equipment described above. The ash specimens were allowed to equilibrate in an environment of air-10 volume percent water at 60°C. Current was continuously monitored versus time under an applied voltage of 2000 volts dc. The tests were operated continuously for 300 to 400 hours. The temperature, voltage and environment utilized were selected to minimize the length of time required to establish a chemical concentration gradient of sufficient magnitude for detection using a simple technique.

After the specimen had been subjected to the above procedure, the ash delineated by the area of the upper electrode was removed in layers about 1 mm thick using a miniature vacuum cleaning device. Each of these layers of ash as well as an equivalent specimen that had not been tested were chemically analyzed. The data were interpreted in terms of changes in chemical concentrations as a function of distance between the positive and negative electrodes. Inherent characteristics of the ash and the difficulty encountered in separating the ash into uniform layers allow only a semi-quantitative evaluation of the data.

Resistivity

$$\rho = V/I \cdot A/l \qquad (1)$$

ρ = resistivity in ohm-cm

V = applied voltage in volts

I = measured current in amperes

A = effective electrode area in cm^2

l = specimen thickness in cm.

Porosity of Resistivity Specimen

$$P = [(V_e - W/d_h)/V_e] \times 100 \qquad (2)$$

P = percent porosity

V_e = volume of lower electrode in cm^3

W = weight of ash occupying V_e in grams

d_h = helium pycnometer density of ash in grams/cm^3

Surface Area Factor for a Unit Volume of Ash

$$S = s \cdot N \qquad (3)$$

S = area in cm^2 of 1 cm^3 of ash

s = surface area of a single ash particle having the mass-median diameter of the ash

$$N = \frac{1 - P/100}{\alpha \cdot d_m^3} \qquad \text{(Reference 4)} \qquad (4)$$

N = total number of particles occupying 1 cm^3 if all are equal to the mass median diameter

P = percent porosity

α = shape factor; $\pi/6$ for spheres

d_m = mass median diameter of the ash.

Atomic Percentage of Elements

After deleting the loss on ignition value, the chemical analyses reported as oxides were normalized to 100 weight percent. Each normalized weight percentage of oxide was divided by the respective molecular weight to obtain molecular decimal fractions. From these values the molecular percentage of each oxide was calculated. The atomic percentage of cation was calculated by multiplying the molecular percentage of the oxide by the number fraction of cations in the given oxide.

SECTION VI
RESULTS

CHARACTERIZATION OF ASHES

The results of microscopic, X-ray and microprobe analyses can be collectively summarized as follows. Over 80 percent of the ash was made up of spherically shaped, glassy particles. Within particles and among particles, chemical heterogeneity can be exhibited. From 5 to 20 percent of the ash consisted of unburned carbon and crystalline compounds.

Table 1 shows the chemical analyses for the various ashes used in this study. The sufficient variation for each reported element suggests that as a group the ashes represent a reasonable cross-section of compositions suitable for this study. Other important ash characteristics are shown in Table 2. Helium pycnometer density values were used to calculate resistivity specimen porosities. Porosity values and the mass median diameter values were used to calculate the surface area factors as shown in the previous section. While not a precise characteristic, the surface area parameter proved useful in analyzing resistivity data as a function of ash composition.

Table 1. CHEMICAL ANALYSES OF ASHES IN WEIGHT PERCENT

Ash No.	Li_2O	Na_2O	K_2O	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	P_2O_5	SO_4[a]	Loss on ignition
1	0.02	0.32	3.10	1.04	2.62	20.50	19.60	46.40	1.69	0.60	1.56	2.10
2	0.01	0.35	2.36	1.66	3.72	16.10	17.80	43.30	1.27	0.36	0.93	10.30
3	0.03	0.38	3.34	1.29	1.04	9.70	25.90	49.90	1.98	0.32	0.29	4.40
4	0.03	0.20	0.26	5.76	22.60	4.25	21.00	38.80	1.19	0.32	0.97	0.33
5	0.01	1.84	0.20	12.75	31.00	11.20	14.80	22.00	0.60	0.39	2.19	0.41
6	0.01	0.25	0.89	1.88	11.10	3.71	23.60	55.60	1.56	0.14	0.22	0.74
7	0.04	0.33	3.88	1.57	0.77	10.01	27.50	51.40	1.79	0.32	0.25	1.50
8	0.04	0.29	2.69	0.98	0.64	9.12	29.10	52.00	2.55	0.42	0.15	1.40
9	0.01	2.31	0.91	1.04	12.10	4.23	25.10	49.60	1.39	0.19	0.21	0.45
11	0.02	1.77	1.13	1.93	6.36	4.61	24.60	53.70	1.49	1.06	0.75	1.49
12	0.01	0.25	0.81	2.57	13.30	4.66	23.60	53.60	0.88	0.19	0.19	0.00
14	0.05	0.38	2.99	1.42	1.00	10.91	26.70	49.10	1.87	0.41	0.29	3.20
15	0.03	0.43	2.58	1.00	0.62	5.63	28.10	49.60	2.29	0.39	0.44	0.58
17	0.04	0.28	2.25	1.04	4.55	24.70	21.20	39.80	1.24	0.31	0.43	5.49
18	0.02	1.28	0.78	3.22	9.14	4.85	19.50	55.10	1.79	0.35	0.72	0.93
19	0.02	1.83	1.19	0.94	5.18	3.81	27.16	57.27	1.05	0.17	0.40	0.60
20	0.07	0.27	2.72	0.76	0.38	3.88	29.78	52.74	1.88	0.18	0.28	7.08

[a]Soluble sulfate.

Table 2. MISCELLANEOUS ASH CHARACTERISTICS

Ash No.	Helium Pycnometer Density in gms/cc	Resistivity Specimen Porosity in %	Mass Median Diameter in μm	Surface Area Factor in cm^{-1}
1	2.65	56.5	19	1380
2	2.56	63.4	12	1840
3	2.33	59.1	24	1020
4	2.70	59.5	14	1740
5	3.00	69.8	12	1510
6	2.48	57.6	12	2120
7	2.29	52.5	20	1430
8	2.41	52.7	17	1670
9	2.34	57.4	10	2450
11	2.19	54,5	10	2740
12	2.39	47.4	20	1580
14	2.25	61.9	20	1170
15	2.47	71.5	6	2850
17	2.35	44.1	67	500
18	2.51	56.8	8	3240
19	2.06	57.0	22	1200
20	2.50	74.8	13	1180

TRANSFERENCE DATA

The objective of this facet of the program was to determine whether an alteration in chemical composition occurs in the direction of the voltage gradient, thereby suggesting the participation of certain ions in the conduction process as charge carriers. Two ashes having exceedingly different chemical compositions but similar values for resistivity were selected for the transference study. A portion of the ash specimen was chemically analyzed before the test. After the specimen had been subjected to a 2000 V/cm voltage gradient for several hundred hours at 60°C in an atmosphere of air containing 9 volume % water, the ash was removed in several layers parallel to each other and perpendicular to the voltage gradient. These individual layers of ash were also chemically analyzed.

The data given in Table 3 illustrate the results of these experiments. An obvious migration of alkali metal ions can be seen. The alkali metal concentration has formed a gradient consisting of a value less than the original concentration at the positive electrode to a value greater than the original at the negative electrode. This suggests that the positive alkali metal ions served as charge carriers and were transported to the negative electrode. Such a concentration gradient was not found for the other species analyzed.

Table 3. CHEMICAL ANALYSES OF TRANSFERENCE EXPERIMENTS IN WEIGHT PERCENT

	Li_2O	Na_2O	K_2O	Fe_2O_3	CaO	MgO	SO_4[a]
Before test, Ash 1	0.017	0.31	3.00	21.0	2.6	0.91	1.7
At positive electrode	0.016	0.26	2.88	21.4	2.5	0.87	1.7
Elevation 1	0.017	0.29	2.96	21.2	2.4	0.88	1.7
Elevation 2	0.017	0.38	3.11	21.4	2.6	0.86	1.7
At negative electrode	0.045	0.54	3.80	21.6	2.5	0.87	1.5
Before test, Ash 9	0.01	2.54	0.94	4.2	12.6	0.97	0.24
At positive electrode	0.01	2.53[b]	0.88	4.2	12.3	0.95	0.25
Elevation 1	0.01	2.39	0.90	4.2	12.4	0.93	0.26
Elevation 2	0.01	2.47	0.90	4.2	12.8	0.97	0.24
At negative electrode	0.01	2.70	0.97	4.2	12.6	0.98	0.24

[a]Soluble sulfate.

[b]Probable error.

Utilizing the relative changes in alkali metal concentration and the quantitity of electricity passed during the experiment, it was estimated that a major portion of the charge could be accounted for by the change in composition. These data do not define completely the overall conduction process nor do they prove that no other ions participate. However, the data offer excellent evidence that alkali metal ions are important in surface conduction and that an attempt to analyze surface resistivity as a function of ash chemistry is justified.

RESISTIVITY DATA

The type of resistivity data taken in this research is illustrated in Figure 5. The open circles represent the measured resistivity data from this research. The closed circles were determined from a computer program[5] designed to predict volume resistivity as a function of ash chemistry, temperature, and porosity. These two ashes were selected to illustrate the typical data because they are almost identical in every characterization except that ash 9 contains considerably more sodium. Therefore, it can be suggested that the two order of magnitude difference in surface and volume resistivity was due to a one order of magnitude difference in sodium concentration alone.

To analyze the resistivity data in terms of fly ash composition, the maximum surface resistivity of each ash was selected from curves like those in Figure 5. This particular resistivity value was chosen to avoid the effect of the variation in sensitivity to water vapor pressure among the ashes. The use of resistivity values taken at a particular temperature or water vapor pressure would not alter the result of this research.

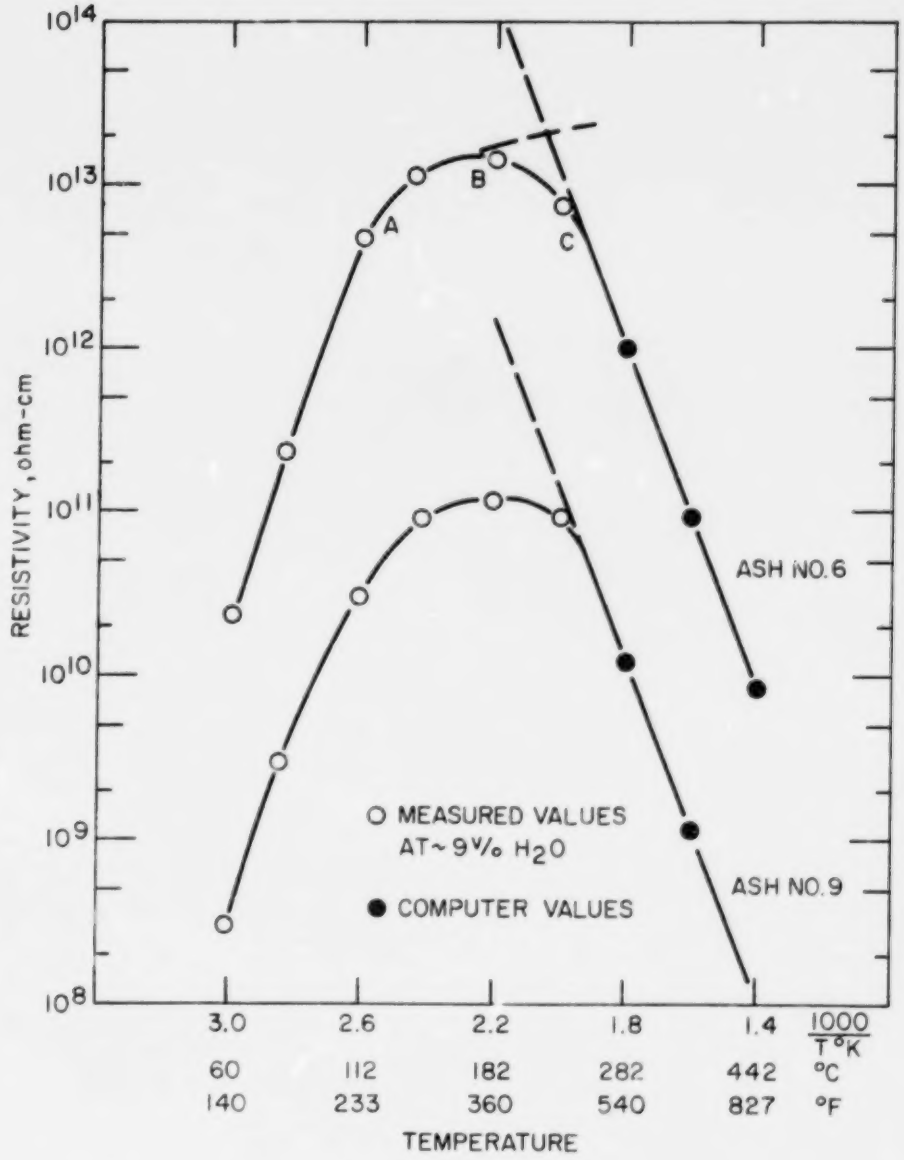

Figure 5. Typical resistivity data as a function of reciprocal absolute temperature

The as-measured maximum or peak surface resistivity was corrected to a common specimen surface area prior to analysis as a function of composition. Ancillary experiments showed that the measured resistance of an ash was inversely proportional to the surface area of the specimen provided ash chemistry was invariant with respect to particle size fraction. All resistivity data were corrected to a surface area factor of 2000 cm^2/cm^3. The surface area factor was calculated as shown by equations3 and 4 in Section V. The basis for applying this correction is detailed in Appendix A.

Other investigators have observed the relationship between surface resistivity and a parameter defining available conducting surface. Dalmon and Tidy[6] related decreasing surface resistivity to increasing specimen bulk density for a specific ash in which case the ash chemistry, theoretical or true density, and particle size distribution were constant.

Since the transference experiments at 60°C indicate the alkali metal ions serve as charge carriers, one would intuitively expect an inverse correlation between surface resistivity corrected to a common surface area and the summation of the three alkali metal atomic concentrations. This correlation failed, indicating the influence of an additional parameter. The situation was clarified when the factors involved were independently examined.

The relationship between surface resistivities normalized to a given surface area and the combined lithium and sodium concentrations is shown in Figure 6. The result was similar to that obtained in a study of volume resistivity.[5] The constructed curve ties together the data for groups of Western ashes having low and moderate amounts of lithium plus sodium. Since the transference experiment showed only a minor migration of potassium for the Western ash and Figure 5 showed the pronounced influence of sodium on resistivity, it is suggested that Figure 6 reasonably illustrates the effect of the combined lithium and sodium.

An attempt to rationalize the lower resistivities for the Eastern ashes based on high potassium content failed. When all the resistivity data in Figure 6 are normalized to a constant value of 0.4 atomic percent lithium plus sodium, and plotted against potassium concentration, the lack of correlation was obvious. This is shown in Figure 7 where the resistivity data for the Western ashes are clustered at one level of resistivity and the data for the Eastern ashes are spread over two orders of magnitude for a narrow band of potassium concentrations. Since the transference data for the Eastern ash indicated a substantial migration of potassium, Figure 7 presents an incongruous result. If one compares the general order of resistivity values for the Eastern ashes in Figure 7 with the chemical compositions of Table 1, it becomes apparent that the iron concentration may be important.

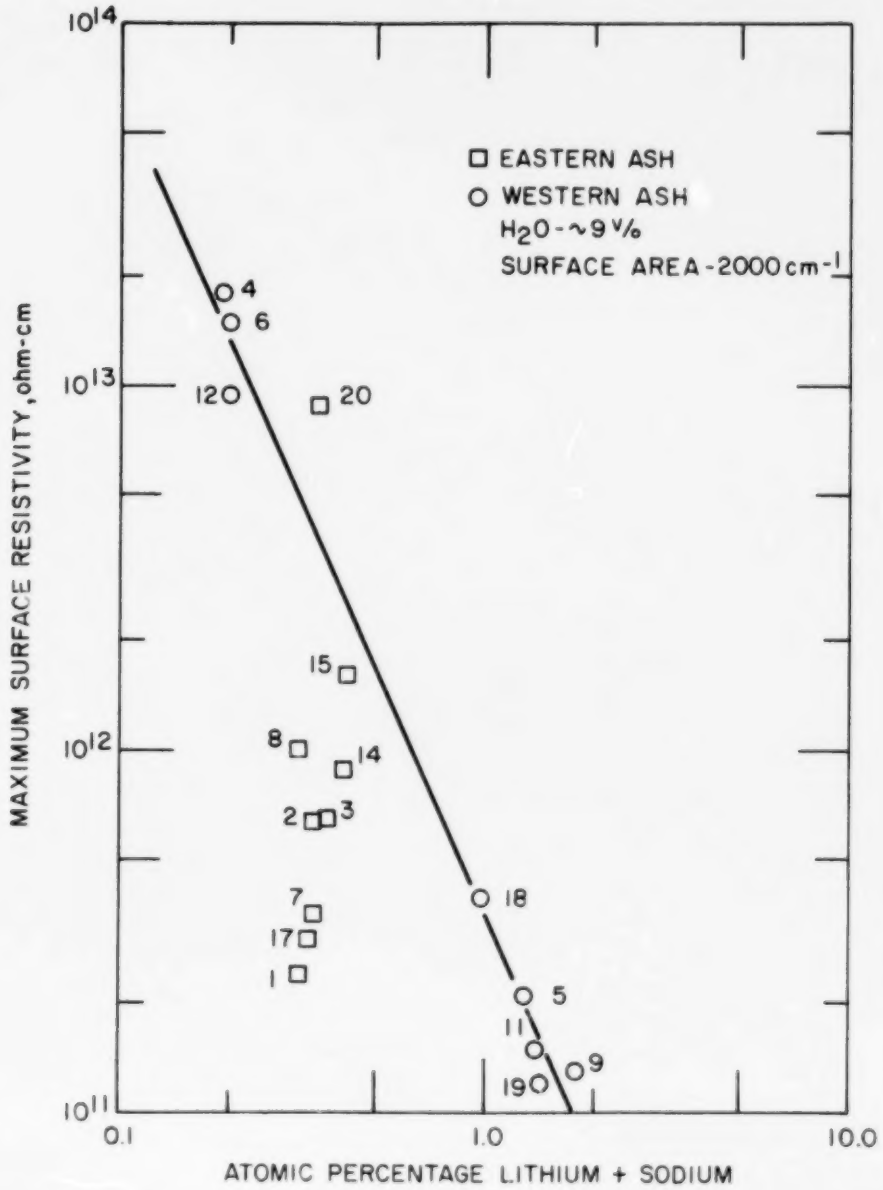

Figure 6. Maximum surface resistivity versus the combined atomic percentages of lithium and sodium

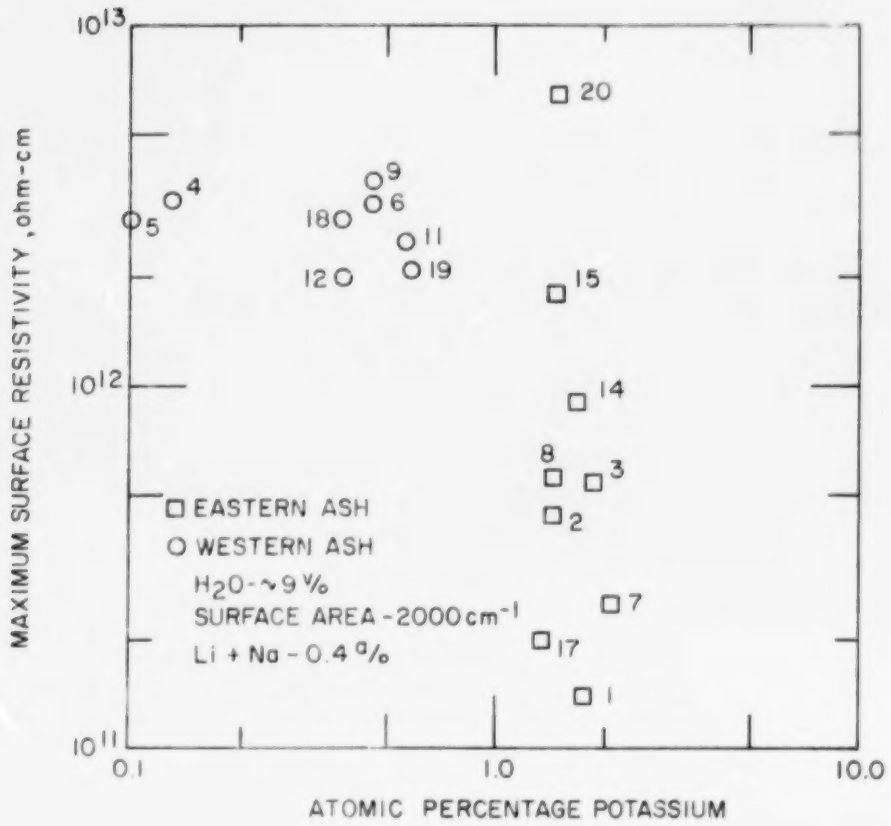

Figure 7. Maximum surface resistivity normalized to 0.4 atomic percent lithium plus sodium versus potassium concentration

In Figure 8 the resistivity data normalized to 0.4 atomic percent lithium plus sodium was plotted against the concentration of iron. A good pseudo-correlation is shown in that iron itself does not participate in the conduction process. It was deduced that iron affects the chemical solubility of the ash, thereby particularly influencing the release of potassium to serve in the conduction process. It was interesting to note that the Eastern ashes 20, 15, 14, 2 and 17 form a straight line. These ashes have similar compositions with the exception of iron content. Also, it was observed that ashes 5 and 7, deviating the most from the constructed line, have respectively the lowest and highest potassium concentrations.

In Figure 9 the relationship is shown for resistivities at constant lithium plus sodium concentration as a function of combined potassium and iron concentration. The correlation is reasonably good as shown; however, if one considers the individual data points with the proposed role of iron and ash solubility as a frame of reference, the correlation is excellent. First, the data for ashes 7 and 14 may represent the expected spread for this type of data. On the other hand, ash 7 contains the greatest amount of total alkali which may also affect ash solubility as well as supply charge carriers. Ash 1 contains by far the greatest amount of soluble sulfate for the high iron ashes and thereby may have lower resistivity due to increased reaction between ash and the environment. Ashes 15 and 20 contain a significant quantity of potassium but are low in iron, thereby limiting the release of potassium. Ash 5 containing a moderate amount of iron possesses very little potassium to support conduction.

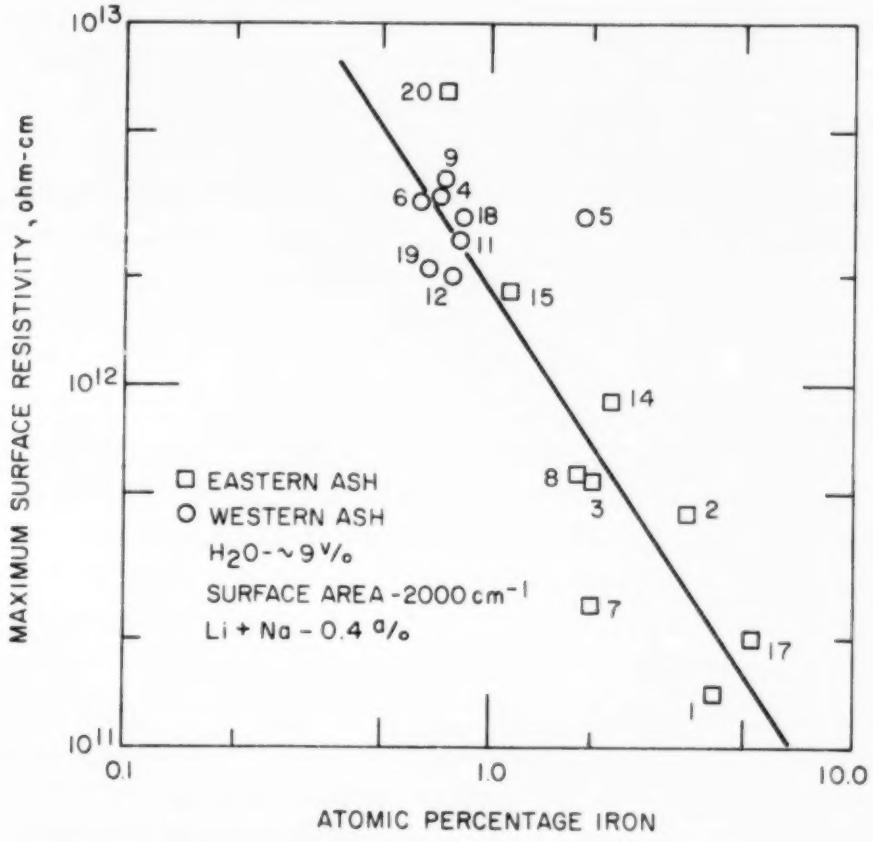

Figure 8. Maximum surface resistivity normalized to 0.4 atomic percent lithium plus sodium versus iron concentration

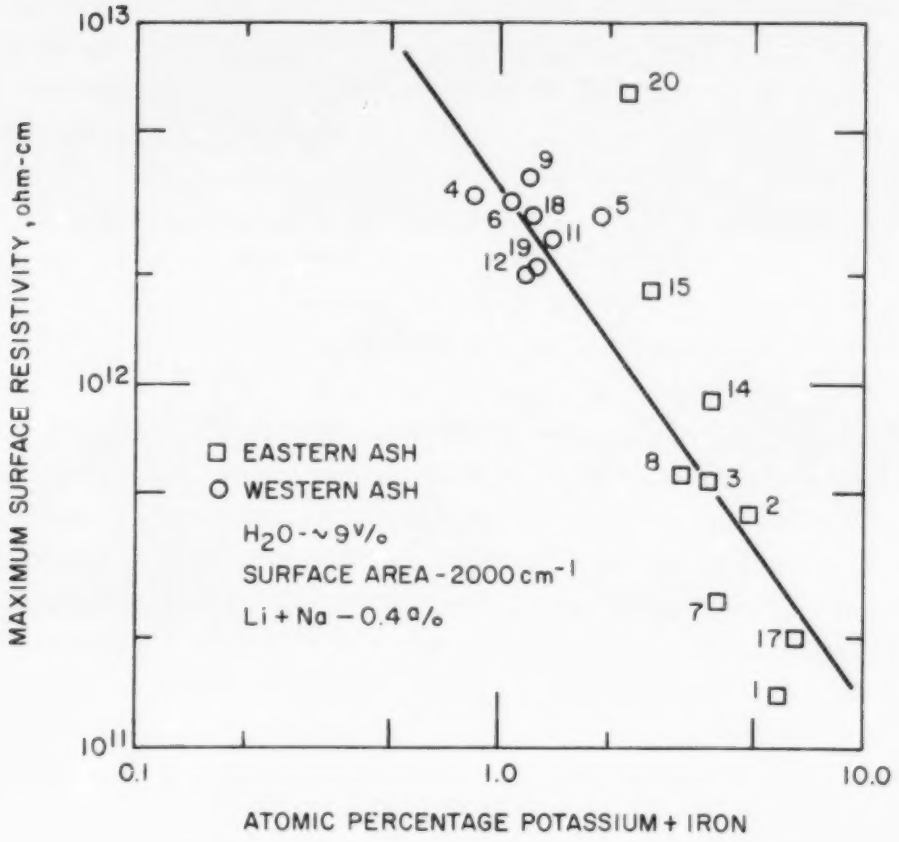

Figure 9. Maximum surface resistivity normalized to 0.4 atomic percent lithium plus sodium versus combined potassium and iron concentrations

SECTION VII
DISCUSSION

SURFACE CONDUCTION

From the foregoing results, it has been observed that alkali metal ions migrate through the fly ash toward the negative electrode under the influence of an applied moderate voltage gradient and conditions suitable for surface conduction. This suggests that these ions have the role of charge carriers and therefore have a pronounced effect on the surface resistivity of the ash. Figure 5 illustrated the magnitude of the effect. Experiments[7] with fused accessory coal minerals have also illustrated the attenuation of resistivity due to the presence of alkali metals. In addition, Selle et al[8] have demonstrated the decreasing surface resistivity of fly ash with increasing sodium concentration.

If the alkali metal ions serve as charge carriers, an inverse correlation should exist between resistivity and some measurement of the available carriers. Without knowledge about the degree of availability for the various carriers, the correlations were attempted using the total atomic concentrations of the alkali metal ions. A correlation between resistivity and the combined concentration of lithium and sodium was readily demonstrated. However, the effect of potassium alone or in combination with the other alkali metals was not detected. Since the transference experiments revealed a minor migration of potassium for one ash and a major contribution by this element for another ash, additional factors of potential influence were considered. It was deduced that the participation of the potassium as a charge carrier was related to the iron concentration of the ash. It is suggested that the presence of iron influences the reactivity between the ash and the environment promoting the dissolution of ash

surface thereby releasing available potassium. Ancillary experiments have shown that the release of the alkali ions in the presence of water is enhanced for ashes of high iron content. Correlations between resistivity and iron concentration or iron plus potassium concentrations were obtained.

The following potential mechanism for the surface conduction of fly ash is suggested by this research. Under appropriate environmental conditions, the ash surface reacts with some agent (for example, water) capable of releasing alkali metal ions from the surface to act as charge carriers. The number of ions released is dependent on: the concentration of available alkali metal ions, the chemical durability of the ash in the hostile environment, the temperature, and the type and concentration of environmental species brought in contact with the ash surface. Tentatively, it would seem that the sodium is more readily released than the potassium. The latter apparently requires more vigorous interaction between the ash and the environment. Although this could be brought about by several of the above mentioned factors, the presence of iron probably by lowering the chemical durability of the ash has facilitated the participation of potassium.

The above discussion principally parallels the explanation of surface conduction for silicate glass. Since the main microconstituent in the ashes examined is a fused or glassy substance, this approach seems justified. Surface conduction for glass is usually explained[9] as an ionic migration of inherent alkali metal ions under the influence of an electric field. Clean, dry glasses containing monovalent cations have exceedingly high surface resistivity. In the presence of a

humid environment, the resistivity decreases slowly at low partial pressures of water, and then rather rapidly as high relative humidity is approached. On the other hand, a very pure, clean siliceous glass maintains a high surface resistivity in a humid environment, indicating the importance of the alkali metals to the conduction process.

Glass containing alkali metal ions can react with water by ion exchange, forming metallic hydroxides (for example, NaOH) which further react with water forming mobile ions on the surface. This process is also in part responsible for the dissolution of glass in water. In addition to the ion exchange mechanism, the glass network itself can be destroyed by reaction with water as well as other agents. The dissolution of the network can permit the accelerated diffusion and migration of ions larger than sodium, for example potassium.

If the suggested surface conduction mechanism for fly ash is essentially correct, it places the role of ash chemistry in the proper perspective and allows one to more objectively consider problems regarding resistivity.

ESTIMATION OF RESISTIVITY

It is conceivable that the figures shown above can be used to estimate maximum surface resistivity from the chemical analysis of ash to anticipate problems for precipitators operating in the region of 150°C. Since the research represents an initial result, the utilization of these data should be approached with caution. Certainly the information will be improved upon with acquisition of additional laboratory data and field information.

A perusal of the individual data points, with respect to the correlations established, leads to the empirical suggestion that about 1.5 atomic percent iron is required to facilitate the participation of potassium in the conduction process. Using this observation, a correlation was developed between estimated resistivity values and those determined in the laboratory. If the ash contained less than 1.5 atomic percent iron, the resistivity value from the curve in Figure 8 for the given iron concentration was determined. This resistivity value was located in Figure 6 at 0.4 atomic percent lithium plus sodium. The intersection of a line, through this point and parallel to the curve in Figure 6, with the ordinate of the known combined lithium and sodium concentration yielded the estimated maximum surface resistivity. For ashes containing more than 1.5 atomic percent iron, the same procedure was used except the starting point was Figure 9 using the combined iron and potassium concentration. The resultant relationship between estimated maximum surface resistivity and the laboratory measured values is shown in Figure 10.

The satisfactory correlation shown in Figure 10 was to be expected since the correlations illustrated in Figures 6, 8, and 9 were reasonably good. Keeping in mind that the resistivity numbers displayed are approximately an order of magnitude greater than those determined in the field, it was interesting to compare the available plant operating experiences with the estimated maximum resistivities. At the plants producing ash having an estimated resistivity $>1 \times 10^{12}$ ohm-cm, all had a high resistivity problem. No problem with high resistivity occurred at plants producing ash with an estimated resistivity of $<5 \times 10^{11}$ ohm-cm. Between these two resistivity values, problems have occurred.

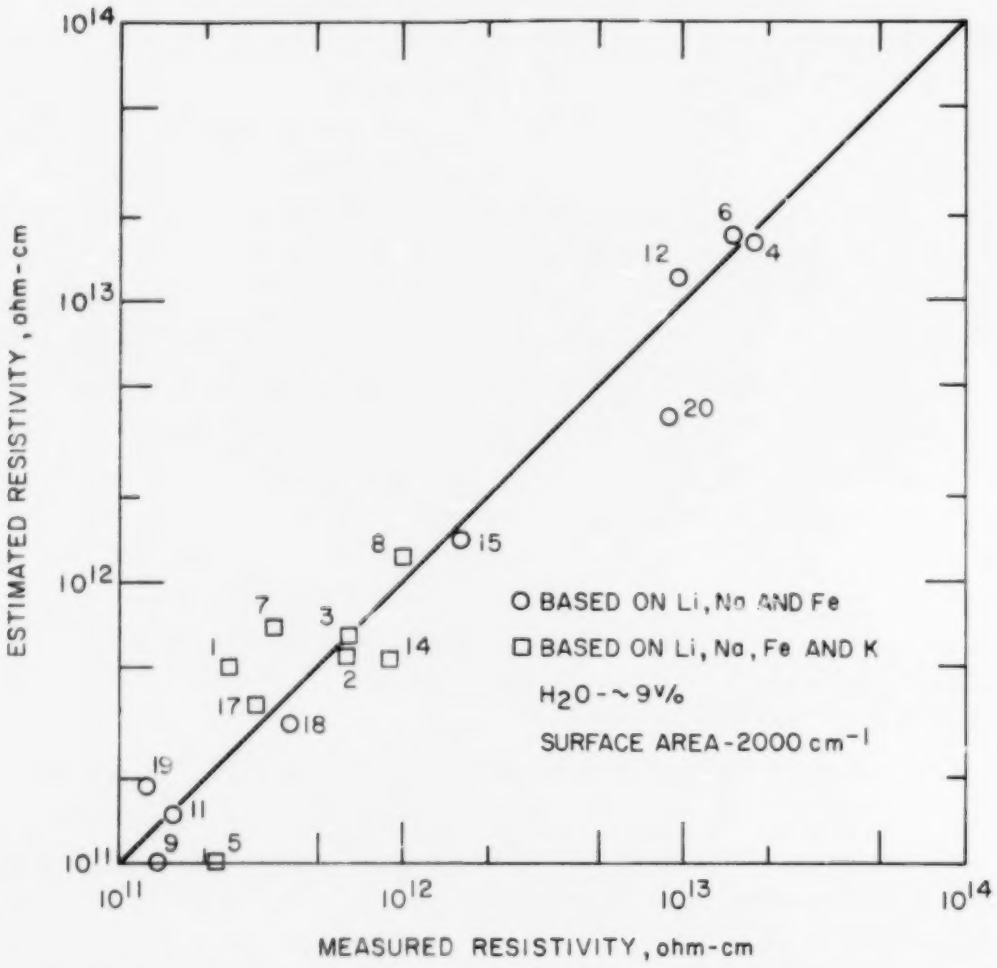

Figure 10. Correlation between estimated and measured maximum surface resistivity

On the positive side, this technique is tailored to a maximum value and ashes possessing wide variations in chemistry, including soluble sulfate, were used. Negatively, the method does not take into account: (1) the magnitude of the effect of water vapor pressure (which at the temperature considered is known to vary with the specific ash), (2) the variation in resistance related to surface area—however, this can be included, (3) the effect of field strength on resistivity, and (4) the effect of variations in environmental or flue gas chemistry. It is hoped that this technique of resistivity estimation will be improved upon and that the influence of the above factors will be investigated.

SECTION VIII
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APPENDIX A
A BASIS FOR NORMALIZING SURFACE RESISTIVITY TO A COMMON SURFACE AREA PARAMETER

In attempting to establish relationships between resistivity and the chemical composition of fly ash, one must consider other factors that can contribute to the magnitude of resistivity. Intuitively the measured surface resistance should be inversely proportional to some measure of the conducting surface area. Since this parameter is inherent for the particular ash, one cannot eliminate the effect but can attempt to take it into account when analyzing resistivity data as a function of ash composition.

A commercial ash was elutriated into five size fractions to examine the effect of a surface area parameter on measured resistivity. All pertinent information for the ash fractions is given in Table 4. Although the chemical compositions for the five size fractions are not invariant, it was believed that the uniformity was sufficient to derive an approximate relationship with which one could normalize surface resistivity to a constant surface area factor. It is obvious that the loss on ignition values are greater for the finer fractions. Shale's[10] work and additional tests in this laboratory indicate that the variation in LOI for a total LOI of < 10% should not influence the results. Comment on the sulfur concentrations will be made below.

Each ash fraction was subjected to the standard surface resistivity test outlined in Section V. A family of surface resistivity versus reciprocal absolute temperature curves were produced similar to those shown in Figure 5. At all temperatures the resistivity was greatest for the coarsest

Table 4. CHARACTERIZATION OF FRACTIONATED FLY ASH

Fraction (μm)	<3	3-7	7-15	15-25	>25
Chemical Analysis					
Li_2O	0.08	0.08	0.08	0.08	0.09
Na_2O	0.48	0.47	0.51	0.47	0.45
K_2O	2.81	2.63	2.81	2.91	2.84
MgO	0.97	0.94	0.98	1.13	1.15
CaO	1.19	1.33	1.12	1.16	1.06
Fe_2O_3	6.89	5.90	8.34	7.69	11.32
Al_2O_3	25.90	26.20	26.80	27.60	27.90
SiO_2	44.90	46.70	48.50	50.60	51.90
TiO_2	1.79	1.45	1.52	1.52	1.63
P_2O_5	0.79	0.51	0.46	0.48	0.38
SO_3 (total)	0.64	0.51	0.28	0.19	0.12
$SO_4^{=}$ (soluble)	0.59	0.41	0.26	0.16	0.07
LOI	8.71	9.05	6.00	3.60	0.87
LOD	0.43	0.18	0.13	0.07	0.07
Helium Pycnometer Density in gms/cc	2.75	2.63	2.56	2.39	2.31
Resistivity Specimen Porosity in %	74.5	67.8	64.7	58.0	54.3
Mass Median Diameter in μm	2.3	3.6	8.0	15.0	40.0
Surface Area Factor in cm^{-1}	6520	5360	2640	1680	690

fraction and lowest for the finest fraction. The three other fractions produced curves between these limits. The only questionable and unexplained data were produced by the 7-15 μm fraction which yielded lower than anticipated resistivity values at temperatures above 125°C. From these curves, the resistivity values at the peak (∿150°C) and at 100°C were taken for analysis.

Surface resistivities as a function of a surface area parameter are shown in Figure 11. The circles represent the maximum surface resistivity, and the triangles represent the surface resistivity at 100°C. It is believed that the linear interpretation of these data points is correct. These data show the pronounced effect particle size (conducting area) can have on resistivity. The effect is greater for lower temperatures. The slope of the curve for data taken at the maximum resistivity position (about 150°C) is ∿ 1.0, for 100°C ∿ 1.5, and for 60°C ∿ 2.0. This increase can be intuitively rationalized since at the lower temperatures more water molecules should spend more time on a given unit of surface.

The data used in this research to evaluate resistivity as a function of ash chemistry were normalized utilizing the above information. Using a slope of one, peak resistivities were adjusted from the measured value at some measured surface area factor to the resistivity the ash would have registered if the surface area factor had been 2000 cm^{-1}. This value was chosen to minimize the magnitude of correction for any one ash.

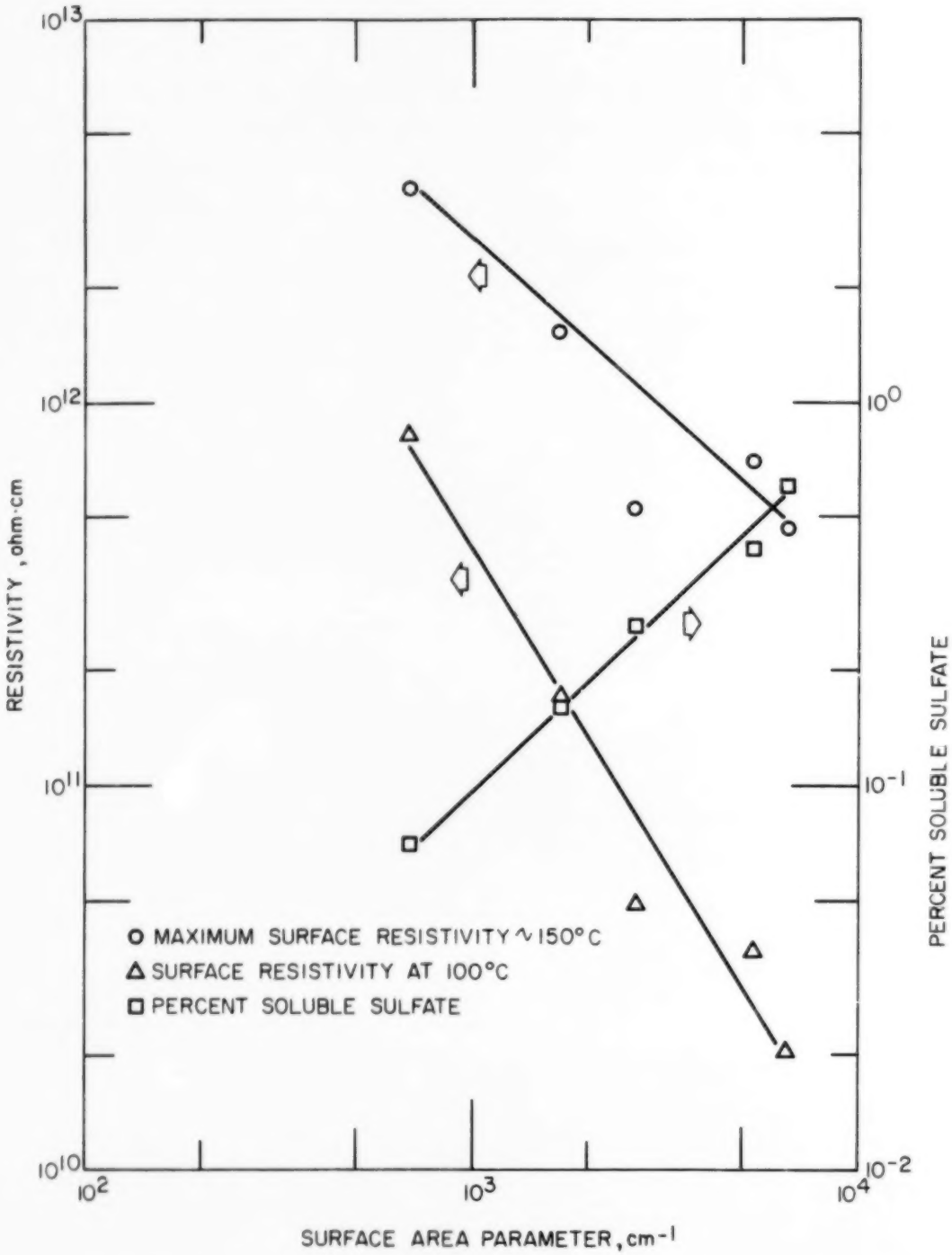

Figure 11. Surface resistivity and soluble sulfate as a function of surface area

In Table IV a disproportionate weight percent of sulfur is found with the finer fractions. This is somewhat misleading. A plot of soluble sulfate versus surface area factor is shown in Figure 11 with a slope of one. This demonstrates that the sulfur which is principally associated with the ash surface is rather uniformly distributed with respect to unit surface area.